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Phase Equilibria for Aqueous Systems Containing Salts and Carbon Dioxide. Application of Pitzer's Theory for Electrolyte Solutions

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PHASE EQUILIBRIA FOR AQUEOUS SYSTEMS CONTAINING SALTS AND CARBON DIOXIDE. APPLICATION OF PITZER'S THEORY FOR ELECTROLYTE SOLUTIONS

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Dedicated to K.S. Pitzer for his 75th birthday

ABSTRACT

The semiempirical specific-interaction model developed by Pitzer is applied to aqueous salt solutions that also contain a dissolved nonelectrolyte. Pitzer's model is used to describe phase equilibria for aqueous solutions containing either sodium chloride and carbon dioxide to 600 bar or sodium sulfate and carbon dioxide to 200 bar at several temperatures. In contrast to predictions reported by previous authors, we find that over wide ranges of pressure and temperature, Pitzer's equations provide an excellent description of salt solubilities in these ternary systems.
Introduction

The semiempirical specific-interaction model (SSIM) of Pitzer \(^1\) has been used extensively to describe the thermodynamic properties of ionic aqueous solutions over wide ranges of concentration, including the region near saturation. For several electrolytes, Pitzer coefficients are available as a function of temperature and pressure \(^2\). For aqueous mixtures of electrolytes, the Pitzer formalism provides a useful predictive tool because it provides the properties of multicomponent mixtures using only information on the binary systems.

However, aqueous mixtures containing both ionic and non-ionic solutes have been studied only rarely within the framework of the Pitzer approach. Pitzer \(^2\) has discussed the dissolution of silica in salt-water systems in terms of the SSIM and recently, Maeda et al. \(^3\) have calculated ionic-strength effects on the dissociation constant of ammonia. Unfortunately in both cases the concentration of the nonionic species is very small and the electrolyte plays the major role. To the best of our knowledge, only Barta and Bradley \(^4\) have used the SSIM to describe gas solubilities in high-temperature brines. These authors also use the SSIM approach to predict the effect of dissolved gases on the solubility of sodium chloride in water.

Recently \(^5\), we have measured the effect of a dissolved gas on the solubility of electrolytes in aqueous solutions. We studied the system \(CO_2-Na_2SO_4-H_2O\) at 50 and 75°C; changes in the solubility of the salt due to \(CO_2\) were described using a simple thermodynamic-consistency procedure which relates this change in salt solubility to the Setschenow constant, that is, to the salting-out of the gas by the salt. In addition to some simplifying assumptions, that procedure requires also information on the ternary system to obtain the derivative of the activity coefficient for the dissolved \(CO_2\) with respect to salt concentration.

The previously-published procedure is capable of describing the observed solubility changes to high \(CO_2\) pressures (150 bar). At higher pressures, the procedure fails, probably because the simplifying assumptions are no longer valid for relatively high concentrations of \(CO_2\) in the aqueous solution.

The previously-published procedure was also applied to the system \(CO_2-NaCl-H_2O\); the solubility of the salt as a function of \(CO_2\) pressure was predicted at several temperatures in the range 50 - 250°C. Predictions at 50°C were confirmed experimentaly. However, the estimated solubilities disagree with those calculated by Barta and Bradley \(^4\), who predicted that dissolved \(CO_2\) increases \(NaCl\)
solubility below 100°C and also above 250°C, while in the range 150 - 200°C, dissolved CO₂ decreases NaCl solubility. Our data at 50°C show that dissolved CO₂ decreases NaCl solubility, and our predictions indicate that this decrease should also be observed at higher temperatures. The discrepancy between our calculated results and those calculated by Barta and Bradley with the SSIM approach prompted us to study the applicability of the SSIM to phase equilibria for aqueous systems containing ions and gaseous non-electrolytes. Our aim in this work is to predict the effect of dissolved CO₂ on the solubility of salts in aqueous solutions using Pitzer parameters obtained from the effect of a dissolved salt on the solubility of CO₂.

Solubility equilibria in gas-salt-water systems

We use in this work essentially the same notation as that used previously ⁵: 0-solvent (water), 1-gas (CO₂), and 2-electrolyte (which dissociates into v⁺ cations and v⁻ anions).

The effect of a dissolved salt on the solubility of a gas (salting in/out) can be described in terms of the activity coefficient γ₁ₓ of the solute, which is given by ⁶

\[ \ln \gamma₁ₓ = \ln \frac{y₁φ₁P}{x₁H₁⁺} - \frac{P}{RT} \int_{P=0}^{P=P⁺} \frac{v₁}{RT} dP \]  

(1)

Subscript x indicates that γ₁ₓ is defined using mole fractions. Here H₁⁺ is the Henry's constant for solute 1 in salt-free water (m₂ = 0), x₁ is the mole fraction of solute 1 in the solution (calculated on the basis of total salt dissociation), y₁ is the mole fraction of component 1 in the vapor phase, v₁ is the partial molar volume of solute 1 in aqueous solution at infinite dilution, \( P^{salt} \) is the vapor pressure of the solvent, and φ₁ is the vapor-phase fugacity coefficient of component 1. Comparing the activity coefficient of solute 1 in salt-free water with that in the electrolyte solution, for the same fugacity of the gas in the vapor, we get

\[ \ln \frac{\gamma₁ₓ}{\gamma₁ₓ^{⁺}} = \ln \frac{x₁}{x₁^{⁺}} - \frac{P}{RT} \int_{P=0}^{P=P⁺} \frac{(v₁ - v₁^{⁺})}{RT} dP \]  

(2)

where superscript ⁺ denotes thermodynamic properties in the absence of salt. Activity coefficients are converted from the mole-fraction scale to the molal scale through
\[ \gamma_1 = \gamma_{1x} \frac{1 - x_1}{(1 + v MW m_2)} \]  

(3)

where \( m \) is molality, \( v = v_+ + v_- \) is the number of ions produced by the dissociation of the salt, and where \( MW \) is the molecular weight of the solvent. In the remainder of this work all activity coefficients are based on the molal scale.

Equation (2) can be compared to the well known Setschenow equation

\[ \ln \frac{x_1^f}{x_1} = k_{21} m_2 \]  

(4)

where \( k_{21} \), the Setschenow coefficient, indicates the effect of salt (solute 2) on the solubility of solute 1.

The equilibrium condition for salt solubility is

\[ \mu_2^s (T,P) = \mu_2^0 (T,P) + v RT \ln (Qm_2 \gamma_2)_{sat} \]  

(5)

where \( \mu_2^s \) denotes the chemical potential of solid salt, \( Q = (v_+ v_-)^{1/v} \), and \( \mu_2^0 \) is the chemical potential of the electrolyte in the standard state. For the aqueous electrolyte, we use the hypothetical standard state of an ideal dilute solution at unit molality at the pressure and temperature of the solution. Using this standard state, the activity of the electrolyte in the saturated solution, \( (Qm_2 \gamma_2)_{sat} \), is a function of pressure and temperature but it is independent of the concentration of any other solute.

From Equation (5) it follows that the solubility of the salt in a solution containing a non-ionic solute can be obtained if we have a method of estimating \( \gamma_2 \). The SSIM provides a simple expression for the activity coefficients of the components in solution.

Pitzer Equations

Pitzer has presented equations for the activity coefficients of the ionic and non-ionic components of an aqueous mixture. For the electrolyte, the mean activity coefficient is given by

\[ \ln \gamma_2 = \ln \gamma_2^* + \frac{2}{v} m_1 (v_+ \lambda_{1+} + v_- \lambda_{1-}) + \frac{3}{v} m_1^2 (v_+ \tau_{11+} + v_- \tau_{11-}) \]  

(6)
\[ + \frac{2v_+v_-}{v} m_1 m_2 (6\tau_{1++} + 3\frac{z_+}{z_-} \tau_{1++} + 3\frac{z_-}{z_+} \tau_{1--}) \]

where \( \lambda \) and \( \tau \) are two-body and three-body interaction parameters respectively, and where \( \gamma_2^* \) is the activity coefficient of the aqueous electrolyte in the absence of solute 1 \((m_1 = 0)\), given by

\[ \ln \gamma_2^* = 1 z_- z_+ |f^Y + \frac{2v_+v_-}{v} m_2 B^Y + \frac{2(v_+v_-)^3 I}{v} m_2^2 C^Y \]  

(7)

where

\[ B^Y = 2\beta^0 \frac{2\beta^1}{\alpha I} \left( 1 - (1 + \alpha I^{1/2} - \alpha^2 I^2 I^2) \exp(-\alpha I^{1/2}) \right) \]  

(8)

\[ f^Y = -A_\phi \left[ \frac{\sqrt{m}}{1 + b \sqrt{m}} + \frac{2}{b} \ln (1 + b \sqrt{m}) \right] \]  

(9)

Here \( A_\phi \) is the Debye-Hückel slope for the osmotic coefficient, \( I \) is the ionic strength, and \( \alpha = 2.0 \) and \( b = 1.2 \). \( \beta^0 \), \( \beta^1 \) and \( C^Y \) are temperature and pressure-dependent Pitzer parameters reported in the literature.

To simplify notation, we define

\[ \Lambda_{12} = (v_+\lambda_{1+} + v_-\lambda_{1-}) \]  

(10)

\[ \Gamma_{112} = (v_+\tau_{11+} + v_-\tau_{11-}) \]  

(11)

\[ \Gamma_{122} = (2\tau_{1+-} + 1 \frac{z_-}{z_+} |v_{1++} + 1 \frac{z_+}{z_-} |v_{1--}) \]  

(12)

The mean activity coefficient of the electrolyte in the mixture is then given by

\[ \ln \gamma_2 = \ln \gamma_2^* + \frac{2}{v} m_1 \Lambda_{12} + \frac{3}{v} m_2^2 \Gamma_{112} + \frac{6v_+v_-}{v} m_1 m_2 \Gamma_{122} \]  

(13)

For the non-ionic solute, the activity coefficient is given by

\[ \ln \gamma_1 = \ln \gamma_1^* + 2m_2 \Lambda_{12} + 6m_1 m_2 \Gamma_{112} + 3m_2^2 v_+ v_- \Gamma_{122} \]  

(14)

where \( \gamma_1^* \) is the activity coefficient of the non-ionic solute in salt-free water \((m_2 = 0)\), given by

\[ \ln \gamma_1^* = 2m_1 \lambda_{11} + 3m_1^2 \tau_{111} \]  

(15)
Activity coefficients $\gamma_1$ and $\gamma_1^{\dagger}$ are obtained from solubility data for the non-ionic solute in the salt-containing solution and in salt-free water, respectively, through Equations (1-3).

Sources of Experimental Data and Evaluation of Parameters

To calculate $\gamma_2$, we use published parameters $^8$ for ionic interactions in binary aqueous electrolyte solutions of NaCl and Na$_2$SO$_4$.

Pitzer et al. $^8$ have given an equation for the chemical potential of solid NaCl as a function of temperature and pressure. That equation, coupled with the SSIM equation for the chemical potential of aqueous NaCl, yields the solubility of NaCl in water, as shown in Table 1. The solubilities at saturation pressure are in good agreement with those reported in the literature $^9,10$. However, because the differences are in some cases close to the limits of the experimental error, we prefer to report the effect of pressure on the solubility through the ratio

$$\Delta m_2^p = \frac{m_2(T,P,m_1 = 0)}{m_2(T,P_{sat},m_1 = 0)}$$

Similarly, we report the effect of concentration of dissolved CO$_2$ through the ratio

$$\Delta m_2^c = \frac{m_2(T,P,m_1)}{m_2(T,P,m_1 = 0)}$$

For aqueous Na$_2$SO$_4$, Holmes and Mesmer $^{11}$ have reported the temperature dependence of $B^\gamma$ and $C^\gamma$ at high temperatures and for the entire range of concentrations at the saturation pressure. Pabalan and Pitzer $^{12}$ have published activity coefficients at high temperatures and 200 bar obtained from heat-capacity measurements. However, the volumetric properties of aqueous sodium sulfate derived from these values are not in agreement with those found in the literature $^{13,14,15}$; for example at 50°C, the reported values of $\gamma_2$ for a three-molal aqueous solution of Na$_2$SO$_4$ give an excess volume of 8 cm$^3$mol$^{-1}$, while direct measurements indicate that it should be about 28 cm$^3$mol$^{-1}$. We therefore prefer to calculate the pressure dependence of $\gamma_2$ from the experimental information available for the partial molar volume of Na$_2$SO$_4$ in aqueous solutions.
We use solubility data for CO₂ in salt-free water reported by Houghton et al., Gillespie and Wilson, Wiebe and Gaddy, and Zawisza and Malesinka. These investigators cover different ranges of pressure and temperature; agreement among them is generally good except for the data of Zawisza and Malesinka, that depart from the other data in a non-systematic way. Malinin has analyzed most of these data and our conclusions agree with his. All the volumetric data required for calculating the activity coefficients of CO₂ in water and in NaCl solutions are taken from Malinin and Moore et al.

To calculate the fugacity of CO₂ in the vapor phase, we use available data for vapor-phase composition at the dew point. Recently, Patel et al. have reported virial coefficients for CO₂-H₂O mixtures to 200°C and pressures to 100 bar at compositions near saturation; these virial coefficients reproduce accurately the data by Wiebe and Gaddy and by Gillespie and Wilson; therefore, we use them for our calculations.

In the range of temperature and pressure where virial coefficients for the CO₂-H₂O mixture are not available, we use the Lewis-Randall rule along with fugacity coefficients obtained from an equation of state for pure CO₂. For the solubility of CO₂ in aqueous NaCl solutions, we use data reported by Malinin et al. and by Takenouchi and Kennedy. These data cover the ranges of pressure and temperature analyzed in this work. A few data by Cramer were discarded because of their poor precision.

The solubility of CO₂ in aqueous Na₂SO₄ solutions has been studied at low temperatures; recently, we reported data at 50 and 75°C.

Calculation of Pitzer Parameters

To obtain Henry's constants in salt-free water, we use solubility, fugacity and volumetric data for the system CO₂-H₂O. The function

$$\ln \left( \frac{y_1 \phi_1 P}{x_1} \right) - \int_{p=1}^{P} \frac{\nu_1}{RT} \, dP$$

is plotted against (1 - x₀); ln H₁ is obtained from extrapolation to (1 - x₀) = 0. Equations (1) and (3) are then used to calculate γ₁ as a function of CO₂ molality,
as shown in Figure 1.

Because \( \ln (\gamma_1 \gamma') \) is a linear function of \( m_1 \) and because the accuracy of the solubility data is not sufficient to determine both parameters in Equation (15), we follow Barta and Bradley \(^4\) and set \( \tau_{111} \) to zero. Table 2 summarizes Henry's constants and \( \lambda_{11} \) for the range 25 - 250°C.

Next, we analyze the available solubility data for \( CO_2 \) in aqueous electrolyte solutions. Equations (2) and (3) are used to calculate \( \ln (\gamma_1 / \gamma_1 \gamma') \). Below 100°C, we assume that the partial molar volume of the dissolved gas in the electrolyte solution remains equal to that in water (i.e. \( \bar{v}_1 = \bar{v}_1 \gamma' \)), so that the second term in Equation (2) can be neglected. Above 100°C, we use the volumetric data reported by Malinin \(^21\). From these data, \( (\bar{v}_1 - \bar{v}_1 \gamma') \) is fixed at -5, -9 and -10 \( cm^3/mol \) for 150, 200 and 250°C, respectively.

There is an important difference between our analysis and that of Barta and Bradley \(^4\). To eliminate explicit \( m_1 \)-dependence, these authors transformed Equation (14) for the activity coefficient of the nonelectrolyte solute \( (\gamma_1) \) and proposed an expansion in terms of the ratio \( (\gamma_1 \phi_1 P / m_1) \). However, the coefficients appearing in these authors' transformed equation for \( \ln (\gamma_1) \) depend on \( m_1 \).

Since the modifications proposed by Barta and Bradley modify the way in which gas concentration is accounted for in the calculation of the activity coefficient of the electrolyte solute [Equation (13)], we prefer to maintain the original virial expansion in \( m_1 \) for the activity coefficient of the nonelectrolyte solute, with pressure-dependent virial coefficients. When the pressure dependence of these coefficients is analyzed, we find that for fixed values of electrolyte concentration, the activity coefficient of \( CO_2 \) is independent of \( m_1 \), as indicated in Figure 2. Therefore, parameter \( \Gamma_{112} \) in Equation (14) can be set to zero.

Finally, parameters \( \Lambda_{12} \) and \( \Gamma_{122} \) in Equation (14) are adjusted by a least-squares regression of the results for \( \ln (\gamma_1 / \gamma_1 \gamma') \) as a function of \( m_2 \). Table 3 gives parameters for the two ternary systems studied here along with the standard deviation of the fit (\( \sigma \)).
Results for the System $CO_2$–$NaCl$–$H_2O$

Table 4 shows the values of the Gibbs energy of solution $\Delta G_{sol}^0$ for $NaCl$ calculated from the equations given by Pitzer et al. $^8$. The mean activity coefficient of $NaCl$ in carbon dioxide-free water is also calculated from these sources; the solubilities of the salt in the ternary mixture at several temperatures and pressures are calculated using

$$\Delta G_{sol}^0 = \mu_2^0(T,P) - \mu_2^o(T,P) = -\nu RT \ln (Qm_2Y_2)_{sat}$$

(16)

by an iterative procedure. Figure 3 shows the effect of pressure on salt solubility. Figure 3 also shows the total, combined effect of pressure and dissolved gas on salt solubility. The curves shown if Figure 3 are calculated with Equation (13) and parameters given in Table 3.

While rising pressure increases the solubility of the salt (except above $200^\circ C$ and high pressure), rising concentration of the nonelectrolyte solute decreases the solubility of the gas. Figure 4 shows the combined effect of $CO_2$ on the solubility equilibria. Between 75 and $100^\circ C$, the effect is smaller than that at other temperatures, but it is always negative, that is, part of the $NaCl$ in solution precipitates as the pressure of $CO_2$ rises. The experimental points in Figure 4 correspond to our measurements $^5$ at $50^\circ C$; they seem to indicate an underestimation of the $CO_2$ effect on the solubility, but they also indicate that the SSIM approach predicts the right sign for the effect. This conclusion disagrees with Barta and Bradley’s assessment $^4$ that $CO_2$ increases the solubility of $NaCl$ at low temperatures.

Moreover, the present results predict that with rising $CO_2$ pressure the decrease of salt solubility is even larger at temperatures above $150^\circ C$. These results are in sharp disagreement with those of Barta and Bradley who predict that rising $CO_2$ pressure increases salt solubility for temperatures above $250^\circ C$.

The different predictions follow from different procedures used to evaluate parameters. The differences in prediction are not due to different sources of experimental data.
Results for the System $CO_2-Na_2SO_4-H_2O$

This system has been studied experimentally at 50 and 75°C. Table 5 presents the volumetric properties of the system and the calculated Gibbs energy of solution of the salt. The procedure for calculation of solubilities is the same as that for the previous system.

Figure 5 shows the effect of pressure on the solubility of $Na_2SO_4$ and the predicted combined effect of pressure and dissolved $CO_2$ on the solubility of the salt. These predictions are obtained with parameters given in Table 3. Taking into account the uncertainties in the SSIM parameters, the observed solubilities are well reproduced by the equations given here over the entire range of pressure (0-200 bar).

Conclusions

Equations (2), (4) and (14) can be combined and rearranged to yield an expression for the Søttschenow constant in terms of Pitzer’s SSIM formalism. Pitzer’s equation for the activity coefficient of the non-electrolyte solute (Equation 14) has three parameters, but we find that for the systems studied here, one of these ($\Gamma_{112}$) can be set to zero. As shown in Table 3, one of the remaining two parameters, $\Lambda_{12}$, is much larger than the other, $\Gamma_{122}$. It follows that $\Lambda_{12}$ is the Pitzer parameter that can most easily be related to the Søttschenow constant for the solubility of a salt in a non-ionic aqueous solution. This parameter is positive for electrolytes that drive the gas out of solution and for gaseous solutes that decrease salt solubility.

The predictions of a previous thermodynamic analysis of solubility coefficients are consistent with those reported in this work, except for the high pressure region where the SSIM approach is superior.
Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No.DE-AC03-76F00098. Additional Funding was provided by the Donors of the Petroleum Research Fund administered by the American Chemical Society.

References

(2) Pitzer K.S., Reviews in Mineralogy 1987, 17, 97.
(21) Malinin S.D., Geokhimiya, 1974, 10, 1523.
TABLES

Table 1 - Measured and calculated solubility of NaCl in water at the saturation pressure

<table>
<thead>
<tr>
<th>T (C)</th>
<th>$m_{2}^{\text{calc.}}$ (calc.)</th>
<th>$m_{2}^{\text{exp.}}$ (exp.)</th>
<th>$\gamma_{2}^{\text{exp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6.145</td>
<td>6.146</td>
<td>1.006</td>
</tr>
<tr>
<td>50</td>
<td>6.279</td>
<td>6.275</td>
<td>1.022</td>
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<td>75</td>
<td>6.355</td>
<td>6.460</td>
<td>0.977</td>
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<tr>
<td>100</td>
<td>6.650</td>
<td>6.680</td>
<td>0.919</td>
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<tr>
<td>150</td>
<td>7.207</td>
<td>7.198</td>
<td>0.724</td>
</tr>
<tr>
<td>200</td>
<td>7.959</td>
<td>7.973</td>
<td>0.503</td>
</tr>
<tr>
<td>250</td>
<td>9.073</td>
<td>8.989</td>
<td>0.299</td>
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</table>

Table 2 - Henry’s constant and binary interaction parameter for the system CO$_2$–H$_2$O at several temperatures

<table>
<thead>
<tr>
<th>T (C)</th>
<th>$H_1^+$ (bar$^{-1}$)</th>
<th>$\lambda_{11}$ (kgmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1655 ± 3</td>
<td>-0.0108 ± 0.0028</td>
</tr>
<tr>
<td>50</td>
<td>2948 ± 3</td>
<td>-0.0335 ± 0.0017</td>
</tr>
<tr>
<td>75</td>
<td>4239 ± 12</td>
<td>-0.0460 ± 0.0027</td>
</tr>
<tr>
<td>100</td>
<td>5335 ± 15</td>
<td>-0.0500 ± 0.0025</td>
</tr>
<tr>
<td>150</td>
<td>6490 ± 20</td>
<td>-0.0501 ± 0.0070</td>
</tr>
<tr>
<td>200</td>
<td>5840 ± 20</td>
<td>-0.0635 ± 0.0124</td>
</tr>
<tr>
<td>250</td>
<td>4420 ± 20</td>
<td>-0.0695 ± 0.0023</td>
</tr>
</tbody>
</table>
Table 3 - Pitzer parameters for two systems

$CO_2$–$H_2O$–$Salt$ at several temperatures

<table>
<thead>
<tr>
<th>T (C)</th>
<th>$\Lambda_{12}$ (kmol$^{-1}$)</th>
<th>$\Gamma_{122}$ (kmol$^{-1}$)</th>
<th>$\sigma$</th>
<th>data ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.114 ± 0.002</td>
<td>-0.0028 ± 0.0003</td>
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<td>19</td>
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<tr>
<td>50</td>
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<td>0.001</td>
<td>17-18</td>
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<tr>
<td>75</td>
<td>0.101 ± 0.003</td>
<td>-0.0029 ± 0.0005</td>
<td>0.010</td>
<td>18-19</td>
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<tr>
<td>100</td>
<td>0.103 ± 0.004</td>
<td>-0.0036 ± 0.0005</td>
<td>0.018</td>
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<tr>
<td>150</td>
<td>0.084 ± 0.007</td>
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<td>0.042</td>
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<tr>
<td>200</td>
<td>0.106 ± 0.002</td>
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<td>0.011</td>
<td>28-21</td>
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<tr>
<td>250</td>
<td>0.091 ± 0.006</td>
<td>-0.0035 ± 0.0009</td>
<td>0.021</td>
<td>28-21</td>
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<tr>
<td>Na$_2$SO$_4$</td>
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<td></td>
</tr>
<tr>
<td>50</td>
<td>0.278 ± 0.022</td>
<td>-0.0034 ± 0.0025</td>
<td>0.059</td>
<td>5</td>
</tr>
<tr>
<td>75</td>
<td>0.272 ± 0.016</td>
<td>-0.0032 ± 0.0018</td>
<td>0.048</td>
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Table 4 - Gibbs energy of solution (divided by RT) of NaCl in water at several temperatures (C) and pressures (bar)

<table>
<thead>
<tr>
<th>$T$</th>
<th>$P_{sat}$</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.776</td>
<td>2.801</td>
<td>2.837</td>
<td>2.871</td>
<td>2.904</td>
<td>2.969</td>
<td>3.030</td>
<td>3.090</td>
<td>3.146</td>
</tr>
<tr>
<td>250</td>
<td>1.997</td>
<td>2.010</td>
<td>2.069</td>
<td>2.126</td>
<td>2.181</td>
<td>2.284</td>
<td>2.380</td>
<td>2.469</td>
<td>2.554</td>
</tr>
</tbody>
</table>

Table 5 - Partial molar volume of Na$_2$SO$_4$ at infinite dilution ($cm^3/mol$) and Gibbs energy (divided by RT) of solution of Na$_2$SO$_4$ in salt-free water at several temperatures (C) and pressures (bar)

<table>
<thead>
<tr>
<th>$T$</th>
<th>$P_{sat}$</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{v}_2$</td>
<td>50</td>
<td>15.0</td>
<td>15.2</td>
<td>15.4</td>
<td>15.6</td>
<td>15.8</td>
<td>16.1</td>
</tr>
<tr>
<td>$\Delta G^o/RT$</td>
<td>50</td>
<td>0.9193</td>
<td>0.8852</td>
<td>0.8501</td>
<td>0.8154</td>
<td>0.7810</td>
<td>0.7129</td>
</tr>
<tr>
<td>$\bar{v}_2$</td>
<td>75</td>
<td>13.9</td>
<td>14.35</td>
<td>14.8</td>
<td>15.25</td>
<td>15.7</td>
<td>16.6</td>
</tr>
<tr>
<td>$\Delta G^o/RT$</td>
<td>75</td>
<td>1.2159</td>
<td>1.1822</td>
<td>1.1491</td>
<td>1.1173</td>
<td>1.0859</td>
<td>1.0256</td>
</tr>
</tbody>
</table>
FIGURES

FIGURE 1
Concentration dependence of the activity coefficient of dissolved CO₂ in water at several temperatures.

FIGURE 2
ln (\(\gamma/\gamma_1\)) as a function of CO₂ concentration in aqueous electrolyte solutions at several NaCl concentrations.

FIGURE 3
Calculated effects of pressure (---) and concentration of dissolved CO₂ (—) on the solubility of NaCl for the system NaCl/CO₂/H₂O at several temperatures.

\[
\Delta m_2^p = \frac{m_2^f(T,P,m_1=0)}{m_2^f(T,P^o,m_1=0)}
\]

\[
\Delta m_2^c = \frac{m_2(T,P^o,m_1)}{m_2^f(T,P^o,m_1=0)}
\]

FIGURE 4
Calculated solubility of NaCl in the ternary system NaCl/CO₂/H₂O at several temperatures. The points show experimental data at 50°C [ref.6].

\[
\Delta m_2 = \frac{m_2(T,P,m_1)}{m_2^f(T,P^o,m_1=0)}
\]
FIGURE 5

Predicted and measured solubility of Na$_2$SO$_4$ for the system Na$_2$SO$_4$/CO$_2$/H$_2$O at 50 and 75°C. The solid curves show the pressure effect. The region bounded by the dashed lines corresponds to the predictions of the SSIM method (with the estimated uncertainty). The solid points show experimental data [ref.5].
NaCl concentration

1.0 ~ 4.5 (mol/kg)

\( \ln(\gamma_1/\gamma_1^*) \)

m_1 (mol/kg)
\[ \Delta m_2^p = \frac{m_2(T,P,m_1 = 0)}{m_2^{\text{sat}}(T,P,m_1 = 0)} \]

\[ \Delta m_2^c = \frac{m_2(T,P,m_1)}{m_2^{\text{sat}}(T,P,m_1 = 0)} \]